Thermally-induced chemistry and the Jovian icy satellites: A laboratory study of the formation of sulfur oxyanions

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[1] Laboratory experiments have demonstrated that magnetospheric radiation in the Jovian system drives reaction chemistry in ices at temperatures relevant to Europa and other icy satellites. Here we present new results on thermally-induced reactions at 50–100 K in solid H2O-SO2 mixtures, reactions that take place without the need for a high-radiation environment. We find that H2O and SO2 react to produce sulfur oxyanions, such as bisulfite, that as much as 30% of the SO2 can be consumed through this reaction, and that the products remain in the ice when the temperature is lowered, indicating that these reactions are irreversible. Our results suggest that thermally-induced reactions can alter the chemistry at temperatures relevant to the icy satellites in the Jovian system. Citation: Loeffler, M. J., and R. L. Hudson (2010), Thermally-induced chemistry and the Jovian icy satellites: A laboratory study of the formation of sulfur oxyanions, Geophys. Res. Lett., 37, L19201, doi:10.1029/2010GL044553.

1. Introduction

[2] Numerous laboratory studies by our group and others [e.g., Moore and Hudson, 2000; Gomis et al., 2004; Loeffler et al., 2006] have demonstrated that magnetospheric radiation in the Jovian system can drive chemical and physical changes in the surface ice of satellites such as Europa. In contrast, it does not appear to be widely recognized that thermally-induced reactions also can occur in ices at temperatures on the order of 80 K even if radiation is not present. Here we report recent experiments on one such set of reactions, namely those involving H2O and SO2, two molecules that are believed to be present on Europa, Ganymede, and Callisto [Lane et al., 1981; McCord et al., 1998a].

[3] Remote sensing of the Jovian satellites has revealed and helped to identify surface materials including H2O ice [Kuiper, 1957; Johnson and McCord, 1971], SO2 [Lane et al., 1981], CO2 [Hansen and McCord, 2008], H2O2 [Carlson et al., 1999a], O2 [Calvin et al., 1996], O3 [Noll et al., 1996], and hydrated materials [Carlson et al., 1999b; McCord et al., 1998b]. Formation of some of these species is readily explained by low-temperature radiolysis of ices. For example, it has been shown that the H2O2 abundance derived from Galileo-NIMS data is consistent with what is expected from a consideration of the Jovian radiation environment and laboratory work on the radiolysis chemistry of H2O2 [Carlson et al., 1999a]. More-recent experiments by Moore et al. [2007] with H2O + SO2 ices demonstrated that their radiolysis at 86 – 132 K produces hydronium (H3O+) and sulfate (SO42-) ions, that after warming under vacuum to remove water, yield H2SO4•H2O. Similar experiments with H2O + H2S ices led to H2SO4•4H2O. The low-temperature observation of H3O+ and SO42-, as opposed to H2SO4, was in keeping with the strongly-acidic nature of the latter and the high abundance of H2O molecules in the ice.

[4] Although the low temperatures of the icy Jovian satellites give little hope for purely thermal chemistry, thermodynamic equilibrium constants (denoted K) nevertheless are suggestive. The acid-base reaction between H2O and CO2, two molecules widely observed in solar system ices, is

\[ 2 \text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{H}_3\text{O}^+ + \text{HCO}_3^- \] (1)

with K \( \approx 10^{-7} \) near room temperature [Soti and Byrne, 2002]. While this value cannot be uncritically applied to cryogenic temperatures, it does suggest that purely-thermal formation of HCO3- is unlikely at \( \sim 100 \) K in H2O-ice. In agreement with this, none of the earlier papers on H2O + CO2 ices [e.g., Sandford and Allamandola, 1990; Hudson and Donn, 1991] reported ion formation. This low equilibrium constant contrasts strongly with the high degree of ionization for the strong acid H2SO4 in water, with K \( \approx 10^9 \) for

\[ \text{H}_2\text{O} + \text{H}_2\text{SO}_4 \rightarrow \text{H}_3\text{O}^+ + \text{HSO}_4^- \] (2)

and a substantial subsequent dissociation of HSO4- into SO42- [Williams and Frausto da Silva, 2000; Lund Myhre et al., 2003]. Correspondingly, our recent ice experiments, described above, showed H2O+, HSO4-, and SO42-, but no detectable H2SO4 until the water was removed [Moore et al., 2007].

[5] We now consider a case intermediate between H2O + CO2 and H2O + H2SO4 ices, namely solid-phase mixtures of H2O and SO2. Sulfur dioxide in aqueous solution reacts according to

\[ 2 \text{H}_2\text{O} + \text{SO}_2 \rightarrow \text{H}_3\text{O}^+ + \text{HOSO}_4^- \text{(and/or HSO}_4^-) \] (3)

with K \( \approx 10^{-2} \) [Scott and Hobbs, 1967], which suggests that this reaction might be observed in ices. Therefore, in the experiments described here we have used infrared (IR) spectroscopy to study solid H2O + SO2 mixtures at temperatures that are relevant to the icy Jovian satellites. We...
J band may be from a bisulfite treated water [4], the presence of deuterium. An alternative assignment, stretching vibrations is also consistent with the D 2 O feature may be a supposition of absorptions from both species in solution should be assigned, showed that the thermal chemistry took place in our ices studied. Since these same bands were unaffected by the presence of deuterium. A similar band has already described. Adding CO2 and CH4 (3-20%) to our H2O + SO2 ices failed to block the growth of the IR features in the 1100 - 950 cm\(^{-1}\) region of Figure 1. Finally, a few D2O + SO2 ices were studied. The IR features shown growing with temperature in Figure 1 were essentially unchanged by the presence of deuterium.

4. Discussion

[16] Figure 1, and the supporting experiments already described, showed that thermal chemistry took place in our H2O + SO2 ices. From reaction (3) we expect the formation of bisulfite on warming a H2O + SO2 mixture, but from there the reaction chemistry becomes complex. Ab initio calculations of Pooele et al. [2004] suggest that the initially-formed species in solution should be HOSO\(_2\), which on further reaction isomerizes to HSO3. Strong support for the latter comes from our observation of a band near 2543 cm\(^{-1}\) (3.93 \(\mu\)m) that grows in with temperature. A similar band has been assigned to the SH stretch in HSO3 by others [Connick et al., 1982; Hisatsune and Heicklen, 1975]. The two features in the 1100 -- 1000 cm\(^{-1}\) region of Figure 1 resemble the bisulfite bands shown in papers of Ermatchkov et al. [2005, Figure 1], and Zhang and Ewing [2002, Figure 3], and Pichler et al. [1997, Figure 1].

[17] All of these earlier papers support an assignment of the 1034 and 1013 cm\(^{-1}\) features of Figure 1 to the S-O stretching vibrations of the two forms of the bisulfite anion, HOSO\(_2\) and HSO3, although it is difficult to say which band corresponds to which anion. Assigning these features to S-O stretching vibrations is also consistent with the D2O + SO2 ices we studied, since these same bands were unaffected by the presence of deuterium. An alternative assignment, proposed by Zhang and Ewing [2002], suggests that our 1034 feature may be a superposition of absorptions from both anions, while the 1013 cm\(^{-1}\) band may be from a bisulfite dimer. The 958-cm\(^{-1}\) feature in Figure 1 agrees with the position of the most intense band of pyrosulfite (S\(_2\)O\(_5\)\(^2-\)), also called metabsulfite and disulfite in the literature. This anion also has a weaker, broader band near 1152 cm\(^{-1}\), which we also observed [see Ermatchkov et al., 2005]. We note that our 958-cm\(^{-1}\) feature is not due to SO3\(^2-\), which we observed at 927 cm\(^{-1}\) on warming ices made of H2O + SO2 + NH3 [Hisatsune and Heicklen, 1975].

[16] To summarize, our observations and spectral assignments are consistent with thermal chemistry that converts SO2 in H2O + SO2 ices into sulfur oxyanions. Although the precise reaction sequence remains unknown, the following path seems reasonable:

\[
SO_2 \rightarrow HOSO_2^- \rightarrow HSO_3^- \rightarrow S_2O_5^{2-} \quad (4)
\]

Formation of S\(_2\)O\(_5\)\(^2-\) is possible through

\[
2 HSO_3^- \rightarrow S_2O_5^{2-} + H_2O \quad (5)
\]

or a similar reaction with the other form of bisulfite [Zhang and Ewing, 2002], or a reaction involving both isomers. The most-likely positive counter-ion in our ices is hydronium (H\(_3\)O\(^+\)), with its IR bands obscured by overlap with those of H2O itself. Comparing the upper and lower traces in Figure 1 (bottom), for before and after anion formation, we find a slight broadening to the left of the H2O-ice feature at 1650 cm\(^{-1}\), in the region where H\(_2\)O, and other forms of the hydrated proton, have an IR absorbance [Kim et al., 2002].

[17] To quantify the conversion of SO2 into ions, we measured the SO2 present in ice samples as a function of deposition temperature and during heating, and assumed that all SO2 lost went into ion formation. Results are presented in Figure 2. The upper panel shows that the amount of SO2 that reacted rose with deposition temperature such that 25 - 30% of the SO2 had formed sulfur oxyanions by 100 K. Figure 2 also shows that for a H2O + SO2 sample made at 50 K, the fraction of SO2 that reacted when the ice was warmed at 1 K/min increased with temperature. By 100 K about 18% of the SO2 had been converted into ions, and the reaction continued at 100 K until the amount converted reached an equilibrium value of about 25%. Figure 2 (bottom) also shows that at the highest temperature (100 K) of these experiments, SO2 sublimation from the ice was negligible, indicating that the decrease in SO2 abundance below 100 K was entirely due to ion formation. The overall result of these measurements is that our H2O + SO2 ices showed as much as a 30% conversion of SO2 into ions by the time 100 K was reached. Total ion abundances on the order of a few percent were achieved. Finally, we note that the ion abundance continued to increase as we warmed our samples to ~150 K, at which point the SO2 band had decreased by 35-40%. However, we cannot discount that a minor amount of the decrease in the SO2 band area could be due to sublimation, and thus this value is an upper limit for the amount of SO2 converted to sulfur oxyanions for the concentrations studied here.

[18] Thermal reactions in H2O + SO2 ics have rarely been mentioned in the literature. In an earlier paper [Moore et al., 2007] we noted IR bands of ions in some of our spectra, without considering their origin and implications. In an older publication by Fink and Sill [1984], the mid-IR spectrum of an ice made of H2O + SO2 + CO2 (80:19:1.2) was presented.

Figure 2. The fraction of SO2 converted into sulfur oxyanions. (top) The fraction converted as a function of growth temperature (solid circle) and during warming from 50 to 100 K at 1 K/min (open circle). (bottom) The fraction of SO2 converted as a function of time during warming from 50 to 100 K at 1 K/min.


